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A STUDY OF GRAFT COPOLYMERS

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A STUDY OF GRAFT COPOLYMERS

Preparation and Viscosity Behavior

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## INTRODUCTION

The study of branching in high polymers is important to the understanding of the relationships between molecular structure and physical properties. It is all the more important because most polymers, even ones usually assumed to be linear, are branched to some extent.

Unfortunately, the determination of the extent, or degree, of branching (that is, the average number of branches per molecule) is seldom easy. The most rigorous method is based on the fact that the size, and hence intrinsic viscosity, is less for a branched molecule than for a linear molecule of the same molecular weight (26,29). The application of this method requires the making of viscosity and light-scattering measurements which are tedious and which require expensive equipment. Another method for the detection of branching has been based upon the determination of Huggins'  $k'$  (14), the slope constant of the curve relating reduced viscosity to concentration; a great deal of empirical evidence has been found indicating a correlation between the presence of branching in a polymer and unusually large values of  $k'$  (10,18,25). Since accurate viscosity measurements can be made readily with fairly simple equipment, this method would, if generally applicable, be very useful.

Since, however, no suitable comparison of these two methods had been made, it was decided to undertake a study of the relationship between Huggins'  $k'$  and the degree of branching as determined from measurements of the intrinsic viscosity and molecular weight of branched and unbranched polymers.

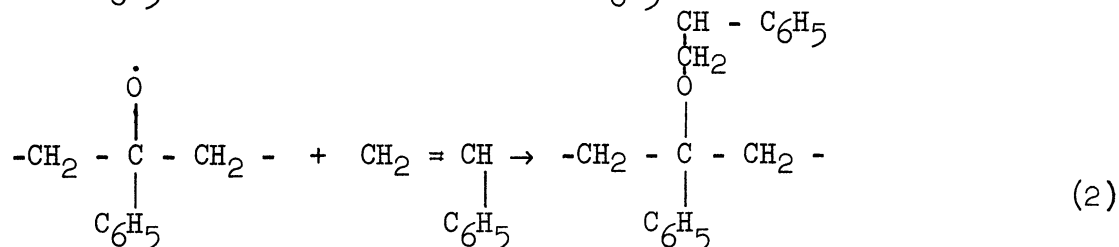
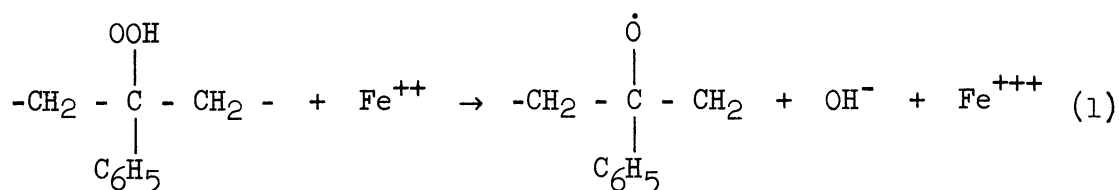
In this study it was desirable to have samples of a high polymer in some of which the molecules would all be essentially linear, while in others each of the molecules would have a known number of linear side chains attached to the main chain. However, most methods available at the time for the preparation of branched polymers with fairly high molecular weights had serious drawbacks.

If one uses polymerization methods involving chain transfer (1,3,13) or copolymerizes a monomer with a cross-linking agent, such as a divinyl compound (6,28), or irradiates a partially halogenated polymer in the presence of its monomer (15,16), one obtains a complex mixture of linear and branched polymers that is often difficult to resolve into its components. Moreover, these methods do not yield polymers with simple branches, but rather encourage the growth of branches on branches or the formation of gel.

The condensation of a monomer with a molecule having a known number of reactive functional groups was used by Schaeffgen and Flory (24) to produce polymers having a known number of branches per molecule, but the average molecular weights obtained were rather low (less than 38,000), and the structure of the branched molecule was unusual (all branches radiating from a single "hub").

By contrast, the technique developed at the Polytechnic Institute of Brooklyn (21) for the grafting of side-chains onto a vinyl-type backbone seemed very attractive. In this method the hydroperoxide resulting from the oxidation of a vinyl polymer is used to initiate the polymerization of a vinyl monomer under redox conditions (see equations 1 and 2). As well as making possible the control of the degree of branching (by varying the degree of oxidation of the backbone polymer),





this method should, in principle, yield a product free of linear material.

Several such graft polymerizations were carried out. The backbone polymers used were polystyrene and copolymers of styrene and 4-vinyl cyclohexene-1 -- the latter because they were expected to oxidize more readily than styrene alone. These polymers were oxidized to varying degrees, and the products were used as initiators in the redox emulsion polymerization of styrene.<sup>1</sup>

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<sup>1</sup> Since this work was first reported at St. Catharines, Metz and Mesrobian have published a report of similar experiments (21); they were, however, unable to achieve satisfactory oxidation of polystyrene itself. Similar studies have also been described by Hahn and Lechtenbohrer (9). In neither case were measurements of Huggins' k' reported.

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In this paper the preparation of the graft polymers is described and evidence that grafting did, in fact, occur is presented and discussed. Finally, measurements of intrinsic viscosity and Huggins' k' are given for the graft polymers and for their fractions.

Other more direct evidence for grafting, based on viscosity and light-scattering measurements, will be given elsewhere (19).

## EXPERIMENTAL

### 1. Materials

Monomers were provided by the Polymer Corporation, Limited, Sarnia. Before use they were freed from inhibitor by washing with dilute aqueous potassium hydroxide, rinsed with distilled water and dried with "Drierite". Cumene hydroperoxide (60%) was also provided by the Polymer Corporation. Phenyl- $\beta$ -naphthylamine and benzoyl peroxide were both practical grade reagents supplied by the Eastman Kodak Company.

Polystyrene samples used for oxidation were prepared by a method described earlier (18); copolymers of styrene and 4-vinylcyclohexene-1 were prepared according to a similar recipe.

Tetralin, of Certified Chemical Grade, was obtained from the British Drug Houses. Other solvents were of technical grade, and were used without further purification.

Inorganic reagents were of Analar Grade, supplied by the British Drug Houses, or of equivalent quality. Nitrogen was purified by passing it first through Fieser's solution (8, p. 395) and then through a saturated solution of lead acetate.

### 2. Oxidations

Solutions of the backbone polymers in tetralin were oxidized at temperatures within the range 70° to 80°C -- usually at 75( $\pm$ 0.2)°C -- by passing oxygen through a sintered-glass bubbling tube in the solution at a rate sufficient to bring about rapid and thorough bubbling without excessive foaming. (No attempt was made to purify the oxygen or to regulate its flow precisely.)

Suitable concentrations ranged from 2 gm/dl for a high molecular weight polymer to 5 gm/dl for a low molecular weight one. In general, the oxidation was more successful with the lower molecular weight polymers.

After bubbling had been continued for a time estimated to correspond to the degree of oxidation desired the product was precipitated in methanol or ethanol. In order to remove tetralin (and its hydroperoxide), the gummy precipitate was reprecipitated several times from a solution in butanone before drying under reduced pressure at 45°C to constant weight. The addition of dry ice to either the solution or the precipitant was found to help in obtaining a porous, easily dried material. Tests showed that with repeated precipitation the observed hydroperoxide content for the precipitated and reprecipitated polymers decreased rapidly at first, but then leveled off to an approximately constant value when a clear, porous product, free from the odour of tetralin, had been obtained.

### 3. Analysis for Hydroperoxide Content

Determination of the peroxide or hydroperoxide content of a high polymer is difficult (2, 27). Although iodometric methods should give values closer to absolute ones than do methods using ferrous ion, the most consistently reproducible results were obtained using the spectrophotometric procedure, based on the oxidation of ferrous ion, which was developed by Laitinen and Nelson (17). Provided that freshly prepared solutions were used, and that a calibration had been made recently, results for various samples of the same polymer were reproducible to within  $\pm 10\%$  in most runs (or, at worst, to within  $\pm 20\%$ ).

In order to see whether or not the spectrophotometric method gave reliable absolute values for hydroperoxide content, the purity of a sample of cumene hydroperoxide was determined. The average value, a mean of 13 determinations, was 108( $\pm 11$ )%, as compared to an average value of 62( $\pm 1$ )% obtained by means of a conventional iodometric titration. Although cumene hydroperoxide is not necessarily a valid standard for the analysis of a high polymer, its structure is similar to that of the polymeric hydroperoxide. It is possible, then, that the values of hydroperoxide content found for the polymers studied are somewhat high.

In this paper hydroperoxide content is expressed as a "hydroperoxide number": the number of hydroperoxide groups per thousand monomeric styrene units.

#### 4. Graft Polymerizations

Graft polymers were prepared in emulsion at 35( $\pm 0.2$ )°C. A typical recipe follows:

Oxidized polymer (in this example, one with a hydroperoxide number of 10)	2.0 gm
Monomer	15.0 gm
Soap flakes	5.0 gm
Water	90.0 gm
Potassium pyrophosphate	2.2 gm
Ferrous ammonium sulfate (hexahydrate)	0.2 gm

Thus, with 2.0 gm of a polymer of hydroperoxide number 10, the amounts of pyrophosphate and ferrous salts listed above were used; with a polymer of higher hydroperoxide content proportionately larger amounts of the salts were used. If more than 15 ml of styrene was required to dissolve the backbone polymer, proportionately more soap and water were used.

First, the backbone polymer was allowed to stand with enough styrene to effect solution. Then the required amount of water was divided into two portions -- one for a soap solution, and one for a ferrous pyrophosphate solution. Both solutions were prepared by heating to 60°C.

As soon as the polymer had dissolved, the two hot solutions were swept out with purified nitrogen, combined, and placed with the polymer solution in a 250-ml bottle fitted with a self-sealing cap. After the contents had been swept out again with nitrogen, the bottles were capped and, by means of a syringe, charged with nitrogen at a pressure of 10 to 15 p.s.i. The bottles were shaken vigorously in order to ensure emulsification, placed in a rack held in a constant-temperature bath, and rotated end-over-end at 33 r.p.m.

When desired, aliquot samples were withdrawn by syringe, and the polymer in them precipitated in methanol containing 0.1% hydroquinone; the percent conversion was determined from the dry weight of the precipitated polymer. When the polymerization was judged to have proceeded to the desired degree of conversion, the contents of the bottles were poured into methanol-hydroquinone solution. After aging overnight, the precipitated polymer was washed with hot distilled water, rinsed three times with methanol, and dried at 45°C under reduced pressure to constant weight.

## 5. Infrared Spectra

Infrared spectra were determined with a Perkin-Elmer recording spectrophotometer, Model 21. Solutions in chloroform of two graft polymers, GC-211 and GC-220, and of two blanks, GC-320 and GC-321 (prepared just as the graft polymers were, except that unoxidized polystyrene

was used in place of oxidized polystyrene), were examined in calcium fluoride cells throughout the range 1200-3800  $\text{cm}^{-1}$ . Spectra for films of samples GC-210, GC-220, GC-250 and GC-320 were obtained independently in the laboratories of the Polymer Corporation Limited.

## 6. Fractionation

The primary fractionation of a graft polymer was achieved by fractional precipitation, at 45°C, from a solution in butanone or in a butanone-benzene mixture, by the progressive addition of methanol or a methanol-butanone mixture. The fractions taken weighed not more than one-fourth of the original weight of the polymer fractionated, and with each polymer the fractionation was continued until at least three-fourths of the polymer had been precipitated.

After each swollen precipitate had been separated, it was carefully washed with a small portion of solvent, and reprecipitated from a solution in butanone. The fibrous product was recovered by filtration, washed with methanol, and dried under reduced pressure at 45°C to constant weight.

## 7. Viscosity Measurements

Values of intrinsic viscosity,  $[\eta]$ , were, unless otherwise noted, determined as described previously (18), by means of the equation of Mead and Fuoss (20):

$$\frac{\ln \eta_r}{c} = [\eta] - \beta [\eta]^2 c \quad (3)$$

Values of  $\ln t_r/c$  (where  $t_r$  = flow time of solution/flow time solvent) were determined and plotted against concentration; since Ubbelohde viscometers having negligible kinetic energy corrections were

used (7),  $\ln t_r/c$  is equivalent to  $\ln \eta_r/c$ . Values of  $k'$ , the slope constant of the Huggins' equation,

$$\frac{\eta_{sp}}{c} = [\eta] + k' [\eta]^2 c \quad (4)$$

were computed from the relation  $k' + \beta = 0.50$ .

## RESULTS AND DISCUSSION

### 1. Oxidations

In Fig. 1 are presented some typical results showing the effect of duration of the period of oxidation on the hydroperoxide content of low molecular weight polymers ( $0.5 < [\eta] \text{ in butanone} < 0.8$ ). Lengths of the vertical lines represent approximately the error in the determination of hydroperoxide number. Although the points are rather scattered, partly because of variations in the rate of flow of oxygen, the data show that the maximum hydroperoxide content was usually reached after oxidation had proceeded for 8-12 hours.

In order to find out whether degradation had occurred during oxidation, the intrinsic viscosities of several polymers were determined before and after oxidation. No decrease in intrinsic viscosity was observed, and it was concluded that degradation had not occurred.

The data in Fig. 1 confirm the importance of the solvent to the oxidation (22). While relatively high hydroperoxide contents were obtained for polymers oxidized in tetralin (which is itself readily oxidized to its hydroperoxide under the conditions used here), hydroperoxide numbers for polymers oxidized in m-xylene were very close to those found for unoxidized polymers.\*

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\* As mentioned above, care was taken to remove residual tetralin from the oxidized polymers.

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It is also clear that pure polystyrene is not readily oxidized by molecular oxygen (9); the highest hydroperoxide number obtained was 9, corresponding to a hydroperoxide concentration of about one mole percent.



In the hope of obtaining higher hydroperoxide numbers, several modifications of the procedure were tried:

1. The use of copolymers of styrene and 4-vinylcyclohexene-1, the oxidation of which should be unaffected by the steric effects encountered with pure polystyrene (22).
2. The use of partially isopropylated polystyrene.
3. The use of catalysts, such as benzoyl peroxide or cumene hydroperoxide.

However, none of these modified procedures gave values of hydroperoxide content greater than 18. Although this value, the highest observed, was obtained with a styrene-vinylcyclohexene copolymer, no correlation was found between hydroperoxide number and vinylcyclohexene content.

## 2. Evidence for Grafting

### a. Conversion Studies

Proof that the polymeric hydroperoxides initiated the rapid polymerization of styrene was obtained from measurements of the percent conversion of styrene to polymer as a function of time. Conversion data for a typical graft polymerization, GC-140, are given in Fig. 2; for comparison, data are included for a blank polymerization, GC-141, a duplicate of GC-140, except for the omission of oxidized polymer from the polymerization recipe. After one hour of reaction, only a small amount (< 3%) of the initial styrene had been polymerized in the blank whereas in the same period more than half of the initial styrene in the graft polymerization had been polymerized.

As the polymerization proceeded, the conversion data tended to become scattered, probably because the emulsion had usually broken

within the first three hours and it was consequently impossible to take truly representative samples. However, the value of percent conversion for the total polymer (corresponding to the last point in the curve for GC-140) always fitted in well with values found for aliquot samples taken during the early stages of polymerization.

Further evidence for the initiation of polymerization by the polymeric hydroperoxides is given in Tables I and II, in which are summarized polymerization and conversion data for several series of graft polymers, and for a number of "blank" polymers prepared (with one exception, GC-141) by replacing oxidized polymer with ordinary polymer.

Without exception, a larger proportion -- usually a much larger proportion -- of the styrene was polymerized with oxidized than with ordinary polymer. (The relatively low conversions in polymerizations GC-161 to GC-200 may be due to their low hydroperoxide content of the backbone polymers used in these runs, but, in general, no close relationship between percent conversion and hydroperoxide content is evident.) These data also indicate no correlation between the vinylcyclohexene content of the backbone polymer and the percent conversion.

b. Disappearance of Hydroperoxide Groups

The evidence just cited indicates that, under the conditions of our grafting experiments, the formation of polymer is initiated by the hydroperoxide groups in the parent (or backbone) polymer. Other evidence of this was obtained from measurements of hydroperoxide content before and after polymerization. Results of such measurements are assembled in Table III. The formation of new polymer in the presence of the parent polymer must yield a product whose hydroperoxide number

(the number of hydroperoxide groups per thousand monomer units) is less than that of the parent polymer. This would be true regardless of whether or not the new polymer is attached to the old. If none of the hydroperoxide groups on the backbone chain were used up in initiating new polymer growth, the hydroperoxide number of the product would still be less because the number of monomer units in the polymer would be increased. In column III are listed the values of hydroperoxide number calculated on the assumption that the decrease is merely due to this "dilution" effect\*; in column IV are the values actually observed.

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\* The following equation was used for the calculation:

$$\frac{\text{wt. } (\underline{\text{bb}}) \times \text{hydroperoxide no. } (\underline{\text{bb}}) + \text{wt. } (\underline{\text{ps}}) \times 0.50}{\text{wt. graft polymer}}$$

where the subscripts bb and ps refer to backbone polymer and polymerized styrene, respectively. For convenience, it is assumed that the hydroperoxide number of the polymerized styrene is 0.50, a reasonable value slightly lower than the average of 0.55 found for the blanks GC-320, GC-321, GC-322, and GC-323; choice of an even lower value would not affect the conclusions.

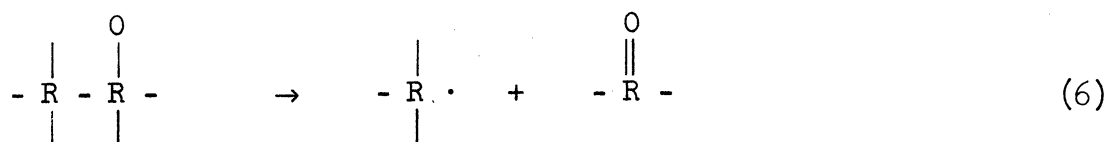
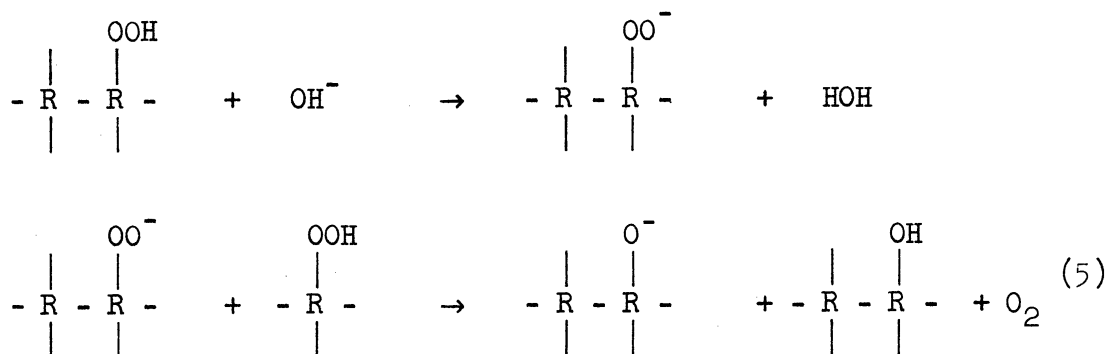
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Even after allowance is made for the rather imprecise results obtained in these analyses, it is clear that hydroperoxide groups do disappear in these graft polymerizations. The precautions taken to remove residual tetralin hydroperoxide were such that at worst the contribution of tetralin hydroperoxide to the hydroperoxide number of the backbone polymer would be less than 1. The polymerization must, therefore, have occurred mainly at the polymeric hydroperoxide sites.

c. Absence of Side-Reactions

So far in this discussion it has been assumed that in the presence of an excess of monomer a polymeric hydroperoxide group disappears by the series of reactions outlined in equations (1)

and (2), rather than by such polar or radical side-reactions as the following:



The occurrence of reactions represented by equations (5) and (6) would result in the disappearance of hydroperoxide groups, and, in the case of the free-radical reaction, in the formation of free radicals that would initiate the formation of linear polymer. Experimental evidence for the occurrence of these side-reactions was sought for, but in vain.

That a polar decomposition induced by the alkaline nature of the emulsion did not occur was demonstrated in the following way. Emulsions of two different polymeric hydroperoxides were prepared, following the recipe for graft polymerizations in all respects except that the ferrous salt was omitted, and rotated in the constant temperature bath for 1.5 and 1.0 hours, respectively, -- times sufficient in a graft polymerization for the conversion of most of the monomer to polymer. The resulting change in hydroperoxide number was negligible: from 4.9 to 4.6 and from 5.2 to 5.6, respectively. It was concluded that the polymeric hydroperoxides used in this study were stable at the pH existing in the emulsions.

The reaction represented by equation (6) would result in the formation of terminal carbonyl groups. The infrared spectra for graft polymers GC-211 and GC-220 and for blanks GC-320 and GC-321 were carefully examined for the presence of absorption peaks corresponding to the absorption frequency of the carbonyl group (in the range 1720-1730  $\text{cm}^{-1}$ ). Although the carbonyl group is detectable at low concentrations (23), no such peaks were found. The spectra for the graft polymers were in fact identical in this range with those for the blanks. These findings were confirmed by examination of the spectra for films prepared from the graft polymers GC-210 and GC-220, and from blanks GC-250 and GC-320.

These findings, though negative, constitute additional justification for our assumption that, under the conditions of our grafting experiments, hydroperoxide radicals on the parent polymer molecules initiate the growth of polymer branches.

#### d. Fractionation Behaviour

Finally, it should be pointed out that the fractionation behaviour of the graft polymers also indicates that grafting has occurred. In carrying out a primary fractionation of linear polystyrene, it is relatively easy to control the number and size of the fractions. With the graft polymers, however, this was very difficult; once precipitation began, a very slight excess of non-solvent tended to bring down all or most of the polymer. This is the behaviour to be expected if the polymer molecules are all large and branched (as they would be if the polymer chains formed were all attached to a pre-existing backbone chain). It is not the behaviour to be expected if the new

polymer chains were independent molecules, for then there would be the usual wide distribution of molecular weights, and the usual wide differences in solubility.

All of this evidence is consistent with only one conclusion: that in the polymerizations described in this paper grafting had occurred, that is, branched polystyrene molecules had been formed by the growth of polystyrene chains onto a polystyrene backbone chain.

### 3. Viscosity Results

If every, or almost every, hydroperoxide group in the backbone polymer became a point of attachment for a branch, the graft polymer molecules must have been fairly extensively branched. For example, molecules of the backbone polymer for the graft polymer GC-210 (Table I) contained, on the average, 9 hydroperoxide groups per 1000 monomer units, and hence an average molecule of the graft polymer may have had as many as 9 branches per 1000 monomeric units in the backbone chain (i.e.,  $9 \times \frac{DP}{1000}$  branches, where DP is the degree of polymerization of the parent polymer).

It was expected, therefore, that Huggins'  $k'$  would have higher values for the graft polymers than for linear polystyrene. The experimental values did not, however, show this difference. In the (unfractionated) graft polymers they fell within the range characteristic of linear polystyrene (0.39-0.44 in butanone, 0.37-0.39 in benzene), and the averages of the values obtained with fractions also fell within these ranges (see Table IV, reference 19).

Evidently  $k'$  is not measureably affected by the branching present in these polymers. This was an unexpected finding. Even a very little (i.e., 0.01%) divinylbenzene copolymerized with styrene

was found to produce sufficient non-linearity in the polymer to increase  $k'$  appreciably (6,19). Indeed, a great deal of evidence has been accumulated for many different polymers showing that non-linearity in polymers leads to high values of  $k'$ .

A careful re-examination of this evidence discloses, however, that when these increases have been observed the non-linearity of the polymer was due either to a small degree of cross-linking or to branching resulting from reactions which could have led (and probably had led) to branches that were themselves branched. Schaeffgen and Flory (24) have indeed reported a very slight increase in  $k'$  for a branched condensation polymer prepared in such a way as to preclude branched branches, but in view of the errors involved in the determination of  $k'$  it is questionable whether the increase observed (average value of  $k'$  for linear polymer, 0.36, for polymer with 8 branches, 0.38) is significant.

On the basis of the evidence now available, it may be concluded that  $k'$  is affected more by bushy branching than by simple branching. Indeed, it may well be that measurements of  $k'$  could afford a means of distinguishing between different types of branching.

This conclusion seems to be reasonable, for  $k'$  is a function of the segment density in the molecular coil (4), and at the same temperature and in the same solvent, the segment density for a molecule consisting of a backbone carrying a few long branches should be significantly less than that for a bushy molecule, and probably little different from that for a linear molecule of the same weight.

It would seem, then, that what affects  $k'$  is not branching per se but branching of such a type and to such a degree that the

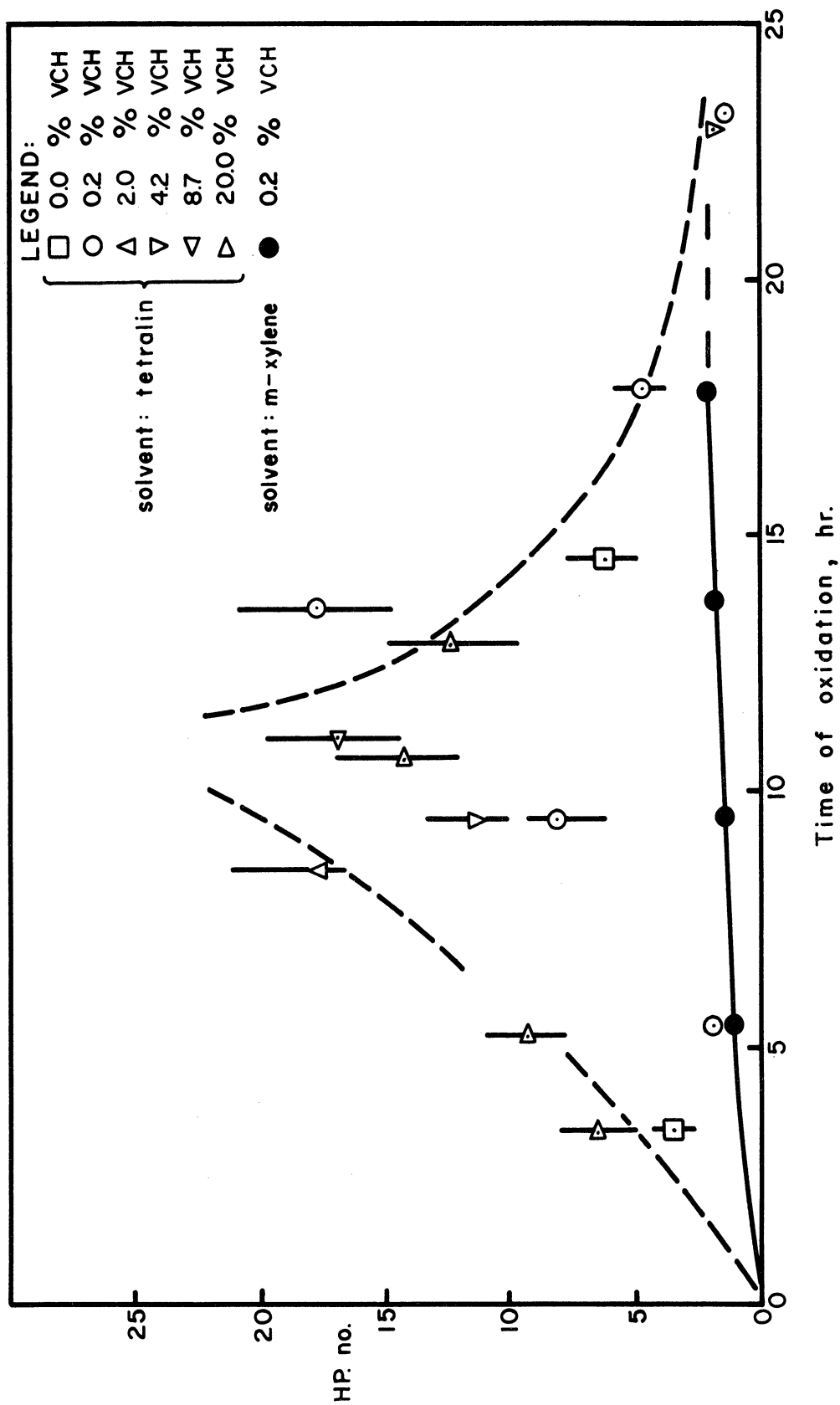
segment density in the molecular coil is significantly altered. Multiple branching (either of the bushy type or of the loose network type) is the kind most likely to increase the segment density. But if the considerable degree of linear branching characteristic of our graft polymers does not affect  $k'$ , it is to be expected that a small degree of multiple branching will not affect it. It is probably for this reason that, to cite two examples, Cragg and Brown (5) found  $k'$  to be normal for low-conversion GR-S, and Hobbs et al. (11,12) found that a high-molecular-weight sample of polyvinyl acetate known to be branched (and probably with bushy branches) gave normal  $k'$  values.\*

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\* It has recently been reported (11) that branching may be detected, by a change in the slope of  $\eta_{sp}/c$  vs.  $c$  curves, when the change in  $k'$  is too small to be detected with certainty. When this method was applied to our graft polymers, an increase in slopes (over that obtained with linear polystyrene of the same intrinsic viscosity) was noted in the curves obtained with benzene solutions but not in those obtained with butanone solutions.

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**Fig. 1** Dependence of Hydroperoxide Content in Time of Oxidation and on 4-Vinylcyclohexene-1 (VCH) content

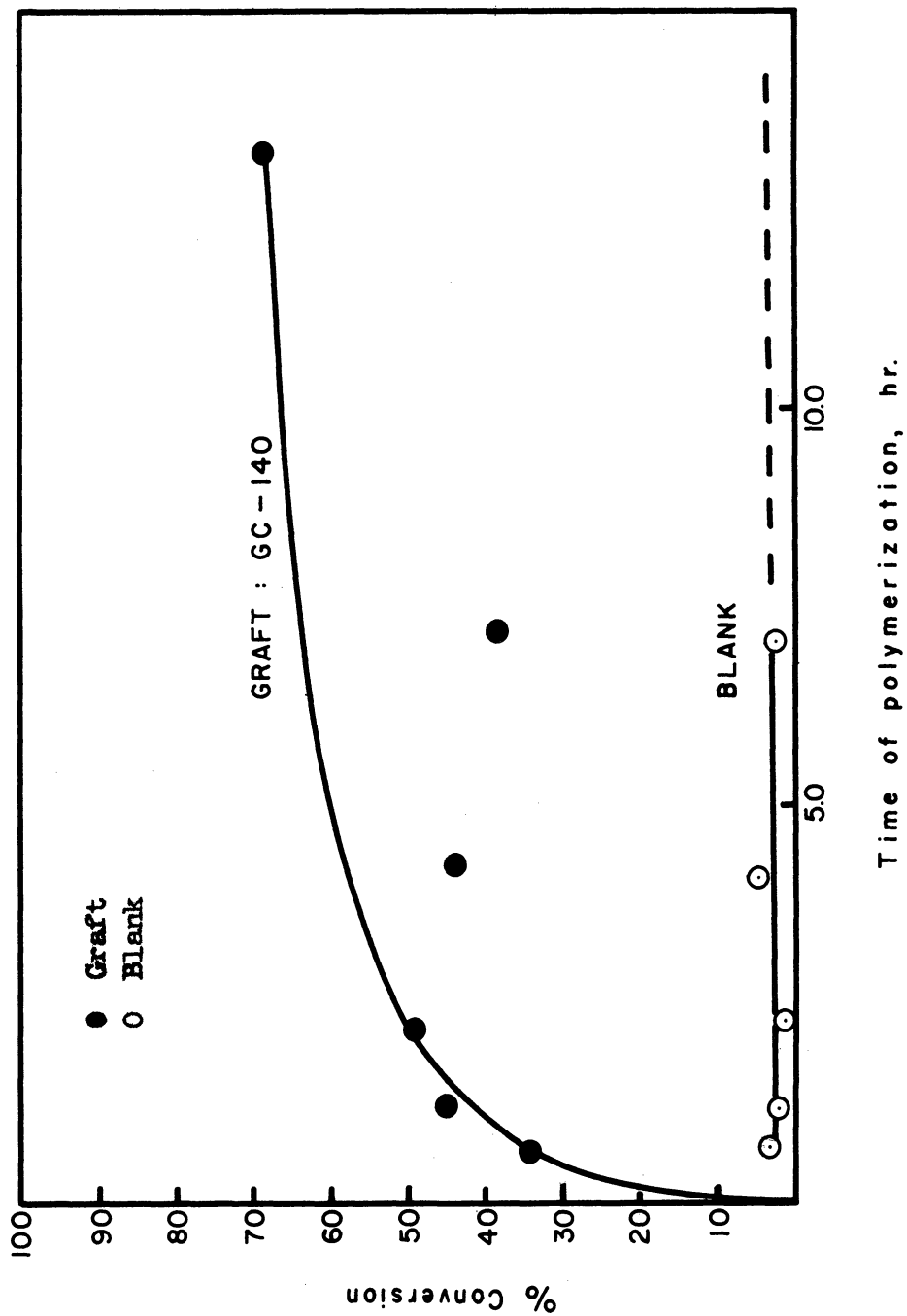


Fig. 2 Dependence of Percent Conversion on Time for a Graft and a Blank Polymerization

TABLE I  
 VISCOSITY AND CONVERSION DATA FOR GRAFT POLYMERS

Sample	% VCH* in Backbone Polymer	HP. no. Backbone Polymer	Weight, gm Backbone Polymer	Styrene	Polymerization Time, hr	Percent Conversion	$[\eta]$ in benzene, dl/gm Backbone Polymer	$[\eta]$ in benzene, dl/gm Graft Polymer
GC-100	0.8	9.5	1.5	10.2	10.0	50	1.70	7.55
GC-110	10.0	18	0.7	14.0	10.0	50	1.13	4.85
GC-140	8.3	7.7	2.0	22.7	13.5	50	1.20	6.54
GC-161	0.0	1.8	1.0	10.2	--	10	--	--
GC-162	0.0	1.8	1.0	10.2	--	10	--	--
GC-163	0.0	1.8	1.0	10.2	--	10	--	--
GC-180	10.0	1.9	1.0	22.7	8.0	10	0.92**	0.95
GC-190	0.4	3.0	1.0	16.4	11.0	10	0.78	2.96
GC-200	0.2	2.0	1.0	11.4	11.0	10	0.82	3.05
GC-210	20.0	9.0	1.0	13.6	9.0	36	0.85**	5.44

\* 4-vinylcyclohexene-1.

\*\* Calculated from value in butanone using relationship given in reference 18.

TABLE I (CONT'D)

Sample	% VCH* in Backbone Polymer	HP. no. Backbone Polymer	Weight, gm Backbone Polymer	Styrene	Polymerization Time, hr	Percent Conversion	$[\eta]$ in benzene, dl/gm	
							Backbone Polymer	Graft Polymer
GC-211	20.0	9.0	1.0	15.0	0.5	82	0.85**	6.43
GC-220	10.0	16	1.0	13.6	9.0	38	0.92**	5.08
GC-230	0.4	7.0	1.0	18.2	9.0	40	3.90	6.05
GC-240	0.4	14	1.0	18.2	9.0	40	3.79	6.19
GC-241	0.4	14	1.0	18.2	1.0	13	3.79	4.19
GC-621	0.0	6.6	0.5	9.1	6.0	15	2.23	6.59

\* 4-vinylcyclohexene-1.

\*\* Calculated from value in butanone using relationship given in reference 18.

TABLE II  
 VISCOSITY AND CONVERSION DATA FOR BLANK POLYMERS

Sample	Weight, gm Polymer	Styrene	Polymerization Time, hr	Percent Conversion	$[\eta]$ in benzene, dl/gm Backbone Polymer	Product
GC-141*	-	22.7	13.5	2.5	--	3.40
GC-250	1.0	18.2	6.0	2.8	1.58	2.38
GC-320	1.0	9.1	5.0	5.6	0.92	1.03
GC-321	1.0	9.1	5.0	2.2	0.92	1.03
GC-322	1.0	9.1	5.0	2.2	0.92	1.02
GC-323	1.0	9.1	5.0	3.3	0.92	1.02

\* This sample was prepared using the same recipe as for GC-140, except that oxidized polymer was omitted.

TABLE III  
DECREASE IN HYDROPEROXIDE CONTENT DURING GRAFTING

Sample	HP. No. of Backbone Polymer	HP. No. of Graft Polymer	
		Calculated*	Observed
GC-100	9.5	2.5	(2.0)**
GC-110	18.4	3.7	0.60
GC-140	7.7	1.4	0.33
GC-180	1.9	0.97	0.86
GC-190	3.0	1.5	1.1
GC-200	2.0	1.2	0.77
GC-210	9.0	2.4	0.57
GC-211	9.0	1.1	0.97
GC-220	16.0	3.4	0.64
GC-230	7.0	1.7	0.27
GC-240	14.0	2.6	0.42
GC-241	14.0	4.4	(3.6)**

\* Calculated on the assumption that none of the polymeric hydroperoxide groups disappear during polymerization.

\*\* Appears to be anomalous.

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Paper Number II

A STUDY OF GRAFT COPOLYMERS

Viscosity and Light-Scattering Measurements

### ACKNOWLEDGEMENTS

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## INTRODUCTION

In the first paper, the preparation and dilute solution viscosity properties of some graft polymers are described. These polymers were prepared by the redox polymerization of styrene in the presence of oxidized polystyrene or of oxidized copolymers of styrene and 4-vinylcyclohexene-1. Evidence that branching had occurred was obtained from measurements of monomer disappearance, of the decrease in hydroperoxide content of the backbone polymer during reaction, and of the infrared absorption by the polymer before and after the grafting procedure. It was then concluded that branched molecules consisting of several long linear branches attached at intervals along a backbone chain had been prepared.

Although the backbone polymer molecules contained an average of up to 12 hydroperoxide groups, each being a potential site for the growth of a branch, values of Huggins'  $k'$  for the graft polymers were no higher than for linear polymers. Since there is considerable evidence that Huggins'  $k'$  is sensitive to small degrees of non-linearity (in polymers branched by cross-linking or by chain transfer), it seemed desirable to obtain, from viscosity and light-scattering measurements, more direct and more quantitative information about the branching believed to be present in the graft polymers. An investigation of this nature seemed even more desirable because of the scarcity of viscosity and light-scattering information about well-characterized branched polymers. A few such studies of cross-linked or randomly branched polymers have been reported (1-6), but no complete study of the effect of simple linear branches on viscosity and light-scattering properties. Although

Jones and others have published light-scattering data for some graft polymers prepared by another method (7), they have not correlated these data with intrinsic viscosities.

In this paper, measurements of intrinsic viscosity and molecular weight, of molecular size, and of the second virial coefficient are reported which confirm the existence of branching in our graft polymers. The data are further used to estimate the degree of branching in the graft polymers.

## EXPERIMENTAL

### 1. Materials

Reagent grade solvents (Eastman Kodak Company) were used for light-scattering measurements; only samples from freshly opened bottles bearing the same lot number were used. The solution of Ludox required for calibration of the photometer was obtained from the E. I. duPont de Nemours Company.

Polystyrene fraction F21 was obtained from the Monsanto Chemical Company; fraction T8 was prepared in our laboratory by Mr. R. H. Sones (8). Fraction Q2B2 was prepared by Mr. B. Waugh using a three-stage fractional precipitation procedure similar to that used previously to prepare fractions F3A2, F5A2, and F7B3 (9). The preparation, and fractionation by means of a single-stage precipitation, of the graft polymers is described elsewhere (10); fraction RP-3-2 was prepared by a similar procedure.

### 2. Methods

The method used for the determination of intrinsic viscosity and Huggins'  $k'$  is described in the first paper in this series (10).

Values of the refractive index increment,  $dn/dc$ , were determined for polystyrene using a Hilger Rayleigh-type interference refractometer; the following values were found for a wavelength of 436 m $\mu$  at 22°C: benzene, 0.111 ml/g; butanone, 0.232 ml/g.

Satisfactory clarification of the organic solvents and polymer solutions was accomplished by centrifuging them in a Servall high-speed angle centrifuge, model SS-1a, for two or three hours at maximum speed (i.e., at about 25,000 g). As long as the dissymmetry ratio,



$I_{45}/I_{135}$ , was 1.03 or less, and as long as very few motes were noted when observed at low angles, the benzene was assumed to be optically clean. Butanone was clarified in a similar way, but gave dissymmetry ratios of about 1.1. Best results in clarifying water were obtained by filtering triple-distilled water first through an ultra-fine sintered-glass filter and then through a Millipore filter disc; the dissymmetry ratio of water cleaned in this way ranged between 1.1 and 1.3. Before use, all equipment such as syringes, cells, and bottles was rinsed six times with clarified solvent, and allowed to dry.

Solutions of different concentrations were prepared for scattering measurements by transferring increments of a concentrated stock solution by means of a syringe to clarified solvent in the scattering cell. Concentrations were determined by weight.

Measurements of light-scattering were obtained using a Brice-Phoenix photometer, series 1000. The photometer was calibrated with solutions of Ludox, the turbidities of which were obtained independently by means of a Beckman DU spectrophotometer equipped with 10-cm cells. The scattering cell was calibrated using dilute fluorescein and found to be symmetrical. As a check of the photometer calibration, the apparent excess turbidity of solution of the Cornell standard polymer in toluene (concentration, 0.5 g/100 ml toluene) was determined. The result obtained was  $3.56 (\pm 0.03) \times 10^{-3} \text{ cm}^{-1}$ , a value in good agreement with results obtained elsewhere (11).

Scattering ratios were measured at 45, 90, and 135 degrees for four or five concentrations of polymer (initial concentration between  $0.9 \times 10^{-4}$  and  $2 \times 10^{-4}$  g/g solution). Corrections were made for the contribution of solvent and for the difference in refractive

index between the polymer solution and the calibrating medium\* (12).

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\* This correction took account of the fact that the receiving slits "saw" past the edges of the incident beam.

---

The so-called "volume" correction and the depolarization correction each amounted to only about 1 %, and were ignored; the correction for reflection of the incident beam, though relatively large when applied to a scattering intensity, was relatively small (< 10 %) when applied to the branching ratio,  $g$ , and was therefore usually neglected.

Following the familiar equation

$$H \frac{c}{\tau} = \frac{1}{MP_{90}} + 2 A_2 c \quad (1)$$

values of  $H \frac{c}{\tau}$  were plotted against  $c$  and the "best" line through the points was extrapolated to zero concentration.  $1/MP_{90}$  was determined from the intercept, and  $A_2$  from the slope. Similarly, values of the dissymmetry,  $z$  ( $z = I_{45}/I_{135}$ ), were plotted against concentration and the line extrapolated to zero concentration to yield the limiting dissymmetry,  $[z]$ . A typical set of dissymmetry and turbidity curves is shown in Fig. 1. The light-scattering data are summarized in Tables I and II. From the values obtained for  $[z]$ , values of  $1/P_{90}$  and  $R/\lambda$  were determined for a random coil with the aid of tables given by Cashin (13). Then values of  $M$  (the weight-average molecular weight) and  $R$  (the  $z$ -average end-to-end length) were calculated.

The following equations give the relationships between the intrinsic viscosity, size, and molecular weight:

$$[\eta] = \Phi \frac{R^3}{M} \quad (2)$$

where  $\Phi$  is the Flory constant (14).

Equation (2) may also be expressed in terms of the root-mean-square radius of gyration,  $S$ . Since  $R^2 = 6 S^2$  for a linear Gaussian coil (14, p. 422),

$$[\eta] = \Phi \frac{6^{3/2} (S^2)^{3/2}}{M} = \Phi' \frac{S^3}{M} \quad (3)$$

where  $\Phi' = 14.7 \Phi$ .

Although it is meaningless to speak of the end-to-end distance of a branched polymer, one may quite properly use the radius of gyration to characterize the molecular dimension. A branching parameter,  $g$ , may now be defined (15):

$$g = \frac{S^2}{S_0^2} \quad (4)$$

where  $S^2$  is the mean square radius of the branched molecule, and  $S_0^2$  the mean square radius of a linear molecule of the same molecular weight. Provided measurements are made in a fairly poor solvent, the following approximation may be made (16):

$$g^{3/2} = \frac{[\eta]_{\text{branched}}}{[\eta]_{\text{linear}} \text{ (same M)}} \quad (5)$$

or

$$g = \frac{[\eta]_{\text{branched}}^{2/3}}{[\eta]_{\text{linear}}}$$

(To be more precise, equation (5) may be modified slightly (16) so that  $g = f(h^3)$ , where  $h^3 = [\eta]_{\text{branched}} / [\eta]_{\text{linear}}$ ).

Assuming that  $\Phi'$  is a constant independent of the degree of branching, we may combine equations (3) and (4):

$$[\eta] = \Phi' g^{3/2} \frac{S^3}{M} \quad (6)$$

Values of  $S$  can be found from a Zimm-type scattering plot, though only  $R$  can be found from simple dissymmetry data. Fortunately, the number found for  $R$  must be less for a branched than for a linear polymer of the same molecular weight; in other words branching can be indicated from the calculation of apparent values for  $R$ , so long as heterogeneity does not mask the decrease in  $R$  caused by branching. It seemed desirable however, to check the consistency of our data by determining  $\Phi'$ . Combining equation (2) with the relationship  $6 S_{\circ}^2 = R_{\circ}^2$ , we have  $S^2 = gR_{\circ}^2/6$ , where  $R_{\circ}^2$  is the mean square end-to-end distance of a linear molecule having the same molecular weight as the branched one being studied. If, then,  $g$  is found from measurements of  $[\eta]$  in a fairly poor solvent (in this case, butanone), and the appropriate value of  $R_{\circ}^2$  is obtained from a plot of  $R_{\circ}^2$  versus  $M$ , an approximate value of  $S^2$  may be readily calculated.

$\Phi$  was calculated from values of intrinsic viscosity, mean square end-to-end distance, and molecular weight;  $\Phi'$  was calculated in a similar manner, except for the substitution of the mean square radius of gyration for the mean square end-to-end distance.

Values of weight-average molecular weight determined for the backbone and graft polymers were used to calculate  $g$  for a model molecule (6); these values of  $g$  were then compared with experimental values obtained from intrinsic viscosities [equation (5); 15, 16]. The model chosen represented a molecule consisting of a linear backbone chain having equally spaced branches of uniform length.

## RESULTS AND DISCUSSION

### 1. Molecular Dimensions

In Fig. 2, the apparent mean square end-to-end distance,  $R^2$ , is plotted against weight-average molecular weight,  $M$ , for fractions of both linear and graft polymers. For the fractions of linear polystyrene, the points fall reasonably well on a straight line, as expected (11). For all the graft polymer fractions, however, the points fall below this straight line.

This effect cannot be due to a greater degree of heterogeneity in the primary graft fractions than in the tertiary linear ones, for a greater degree of heterogeneity should result in a higher, rather than a lower, value of  $R^2$ . For example, the value of  $R^2$  for the linear polystyrene fraction RP-3-2, which was prepared by means of the same one-stage fractionation procedure as used in fractionating the graft polymers, and should therefore be more heterogeneous than the tertiary fractions, falls slightly above the line, not below it.

On the other hand, a branched polymer should give a lower value of  $R^2$  than linear polymers of the same molecular weight (15). The decrease in  $R^2$  observed with the graft polymer is therefore further evidence for the existence of branching--the branching that should result from the growth of polymer from sites along a backbone chain.

It should be noted that the decrease in  $R^2$  (that is, the extent to which a point falls below the straight line in Fig. 2) was less for fractions precipitated first during fractionation than for those precipitated later. This indicates that, in this system at least, the more highly branched fractions are the more soluble.

## 2. Intrinsic Viscosities

Further evidence for branching in the graft polymers may be found in Fig. 3, in which intrinsic viscosity, measured in butanone, is plotted against molecular weight for both linear and graft polymer fractions (on a log-log plot).

The points for the linear polymer fractions fall on, or very close to, a straight line for which the equation has the usual form\*

$$[\eta] = 1.8 \times 10^{-4} M^{0.66}$$

---

\* This equation is very similar to that obtained by Doty, Affens and Zimm (17).

---

By contrast, the points for the graft polymer fractions all, with one exception, fall below this line. The intrinsic viscosity of a graft polymer fractions, in other words, is less than that of a linear polymer fraction of the same molecular weight. This is, of course, the behaviour to be expected if the graft polymers are branched.

The data of Fig. 3 also provide additional evidence for the conclusion that the more highly branched polymer is the more soluble. Generally speaking, the branching ratio  $g$  is higher (that is, the degree of branching is lower) the earlier a fraction precipitates during fractionation. (The numbers beside the points refer to the order in which the fractions precipitated.) This greater solubility of more highly branched polymer has been predicted (19), but it has been reported in only a few systems (20, 21). This may be because branching is usually a result of chain transfer to polymer (or of incipient cross-linking) and then the most highly branched molecules are the largest ones. Here,

in these graft polymer fractions, the molecules are for the most part of about the same weight, and the solubility is determined mostly by the molecular size and hence by the degree of branching.

### 3. The Flory Constant, $\Phi$ or $\Phi'$

Values of  $\Phi$  calculated for the linear fractions are given in Table I. The average value obtained with benzene as solvent is  $2.2 \times 10^{21}$ , which agrees with the value  $(1.9-2.3) \times 10^{21}$  suggested by Flory (14); the average of the two values calculated with butanone as solvent is  $1.9 \times 10^{21}$ . In contrast, individual apparent values of  $\Phi$  found for the graft polymers range from  $2.3 \times 10^{21}$  to  $6.2 \times 10^{21}$  (see Table II). These wide deviations from normal values were not reduced appreciably by using a polydisperse, rather than a monodisperse, coil as a model.

An increase in  $\Phi$  is to be expected if branching is present in the polymer. If these increases are indeed due to branching, substitution of  $S^3$  for  $R^3$  in equation (2) should yield the constant  $\Phi'$ . If, in addition, Flory's assumption (14, p. 611) that  $\Phi'$  has the same value for linear and branched molecules is valid,  $\Phi'$  should equal  $14.7 \times \Phi$ , or  $3.1 \times 10^{22}$  (equation 3). Table III gives values calculated for  $\Phi'$  in benzene for the graft polymers. The values of  $\Phi'$  in the first column were calculated using values of  $g$  determined from equation (5); those in the second column were calculated using values of  $g$  determined by means of the Stockmayer-Fixman method (16). According to the first method of calculating, the average value of  $\Phi'$  is  $3.4 \times 10^{22}$ , which is in excellent agreement with the value expected.\*

---

\* If, on the other hand, we were to calculate  $\Phi'$  on the assumption that the graft polymers are linear (i.e., assume that  $g = 1$ ), the value of  $\Phi'$  obtained would be  $4.7 \times 10^{22}$ .

According to the second (and presumably more reliable) method, the average value of  $\Phi'$  is  $4.5 \times 10^{22}$ --somewhat higher than expected.\*

---

\* There is, however, other evidence in the literature that  $\Phi$  or  $\Phi'$  has a higher value for branched polymers than for linear ones (3, 5).

---

In any case, the use of  $S^3$  rather than  $R^3$  for the graft polymers results in a proportionality between intrinsic viscosity and molecular size that is similar to that for a linear polymer. This similarity is made clear by Fig. 4, in which values of  $S^3/M$  for both linear and graft polymers in benzene are plotted. The close agreement shows that the viscosity, size, and molecular weight data for each sample are mutually consistent, and justifies the use here of dissymmetry measurements rather than complete measurements of the angular distribution of scattering.

#### 4. The Second Virial Coefficient, $A_2$

Further confirmation of the existence of branching in the graft polymers may be found in a comparison of values of the second virial coefficient,  $A_2$ , for linear and graft polymers. As seen in Table I, values of  $A_2 \times 10^4$  for the linear fractions are between 2.6 and 5.4 for solutions in benzene; values are, as expected, lower for solutions in the poorer solvent, butanone.

On the other hand, values of  $A_2 \times 10^4$  for the graft polymers (Table II) range from -0.3 to +1.6 in benzene. In spite of considerable scatter, all of these values fall well below the range of values for linear fractions of the same molecular weight. Such a lowering of  $A_2$  by branching has been predicted (14) and has been observed in several polymer systems (3, 22).



## 5. The Branching Parameter, g

Now that the presence of branching in the graft polymers has been confirmed, the degree of branching may be considered.

As shown in Table IV, values of  $g$  calculated by using equation (5) range from 0.65 to 1.0; values of  $g$  calculated by the more refined Stockmayer-Fixman procedure range from 0.58 to 1.0. By comparing these experimental values with values calculated for the model molecule described earlier the average number of branches per weight-average molecule may be calculated.

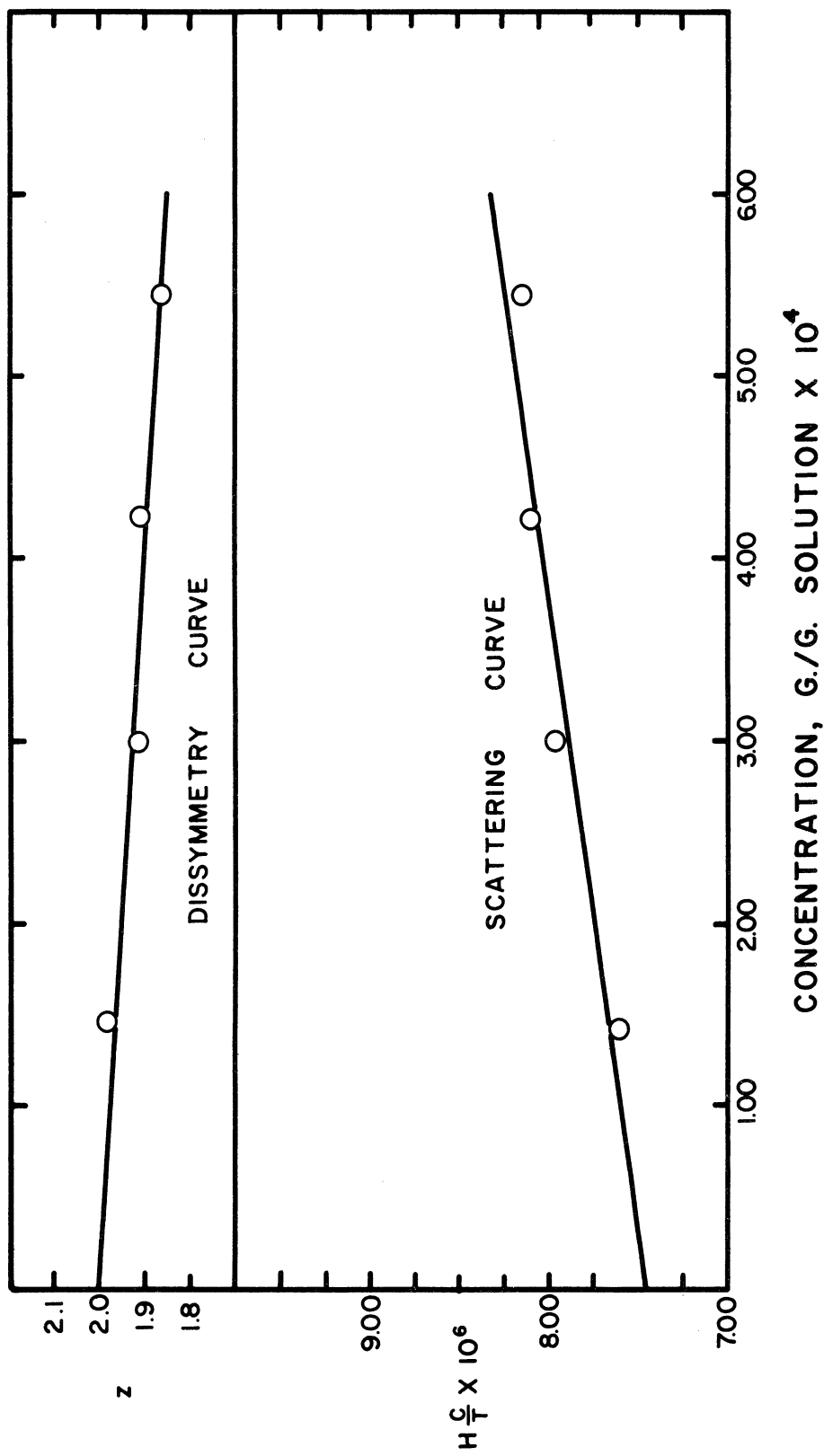
Consider, for example, fraction GC-211-3. The average molecular weight of the backbone chain in this sample was  $1.4 \times 10^{-5}$ . Taking this as the backbone molecular weight for our model molecule we obtain the following values of  $g$  for 2, 4, 6, and 8 branches per molecule, respectively: 0.97, 0.62, 0.40, and 0.35. This observed value for  $g_{(SF)}$ , 0.46 (or the observed value for  $g_{(SF)}$  corrected for reflection, 0.43) corresponds then to molecules having about 6 linear branches equally spaced along the backbone.

Since fraction GC-211-3 has the lowest value of  $g_{(SF)}$  of any of the fractions, we may conclude that the graft polymers contain up to six branches per molecule.

This estimate may be compared with the number of branches calculated by assuming all hydroperoxide groups in the backbone chain took part in the formation of a branch. If the analyses for hydroperoxide content are correct, the backbone chains of this fraction could contain up to twelve hydroperoxide groups, and hence branches. However, as pointed out in the earlier paper (10), our method of analysis may yield high values for hydroperoxide content; the agreement between the two estimates seems satisfactory.

## 6. Huggins' k'

Although it might be expected that the value of Huggins'  $k'$  for the graft polymers would be higher than for linear polystyrene (23), the data in Table IV show that the average values of  $k'$  in benzene or butanone (0.34 and 0.36, respectively) are, in fact, not significantly greater for the graft polymers than for the linear ones (0.35 and 0.39, respectively). On the basis of this evidence, it was concluded in the earlier paper (10) that Huggins'  $k'$  is not affected noticeably by the presence of a few linear branches. Results of the study reported here make it possible to conclude, more quantitatively, that Huggins'  $k'$  seems to be insensitive to the presence of about six branches per molecule. A more detailed discussion is given in the earlier paper (10).



(SAMPLE: GC-210-3)

Fig. 1 Typical Reciprocal Intensity and Dissymmetry Curves for a Graft Polymer

A small number beside a point on the graph indicates the order in which the fraction appeared during fractionation; thus the number 2 placed beside a point belonging to the GC-210 series indicates the second fraction obtained in that series, namely, fraction GC-210-2.

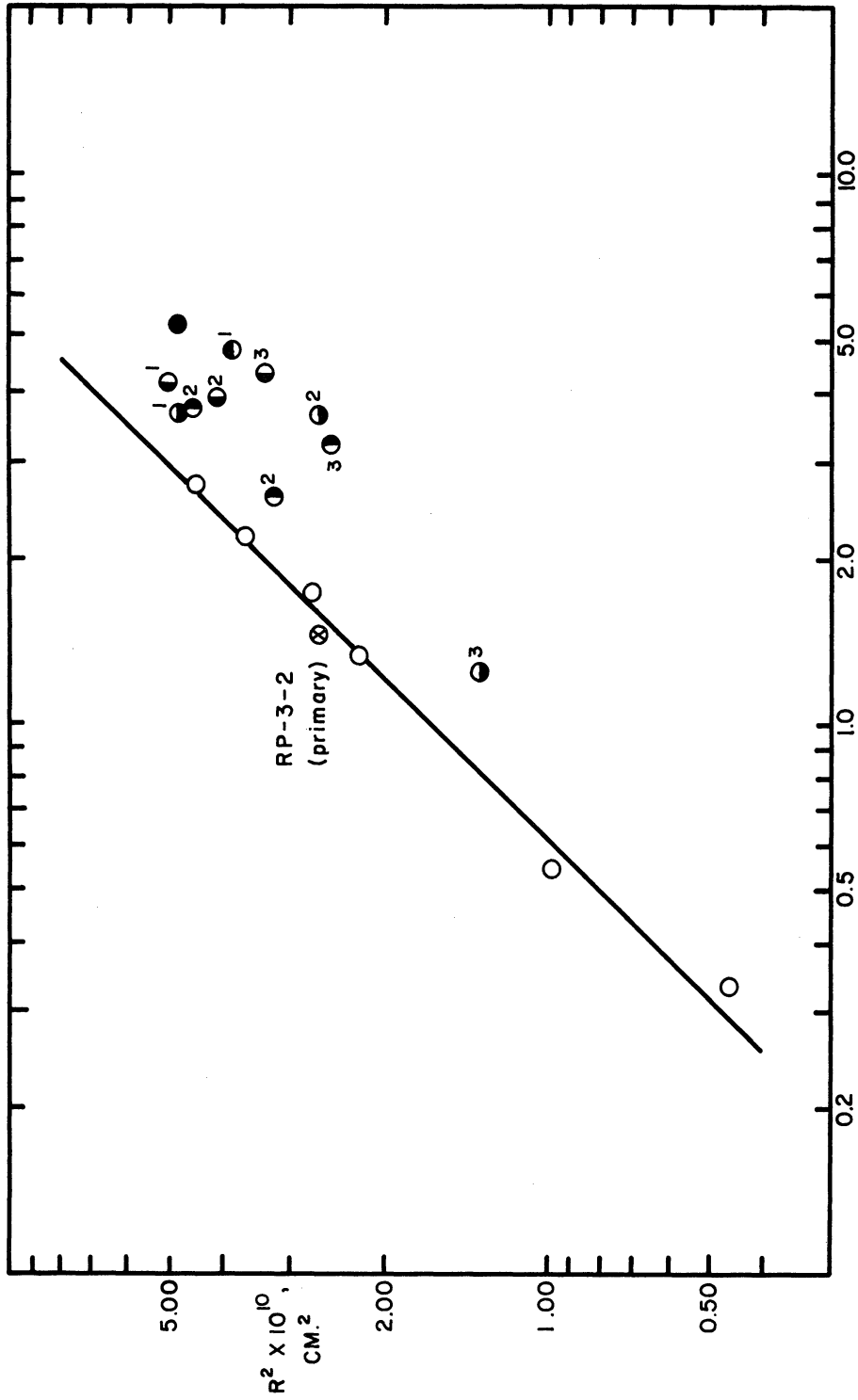


FIG 2

Fig. 2 Dependence of Molecular Dimensions in Benzene on Molecular Weight

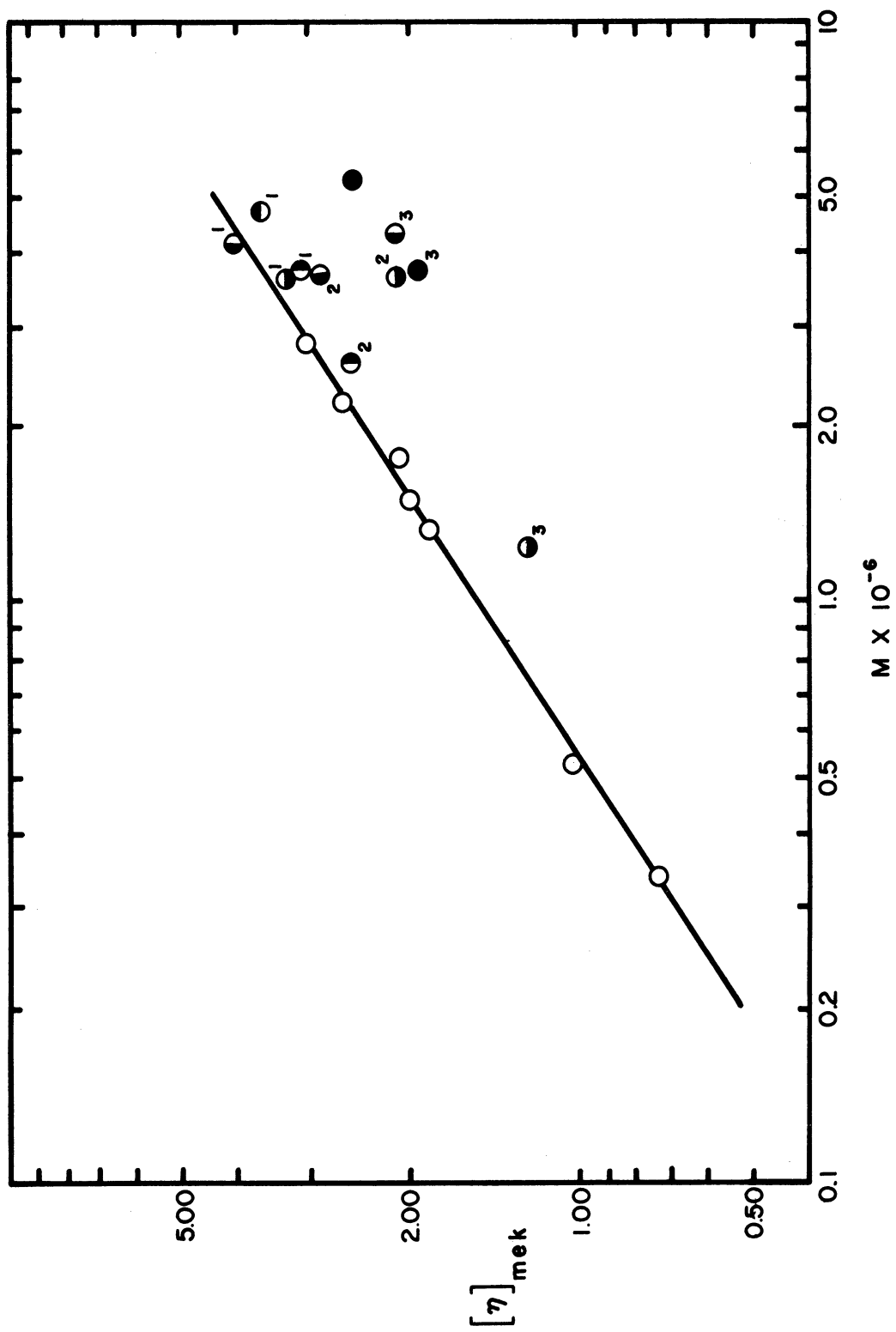


Fig. 3 Dependence of Intrinsic Viscosity (in Butanone) on Molecular Weight

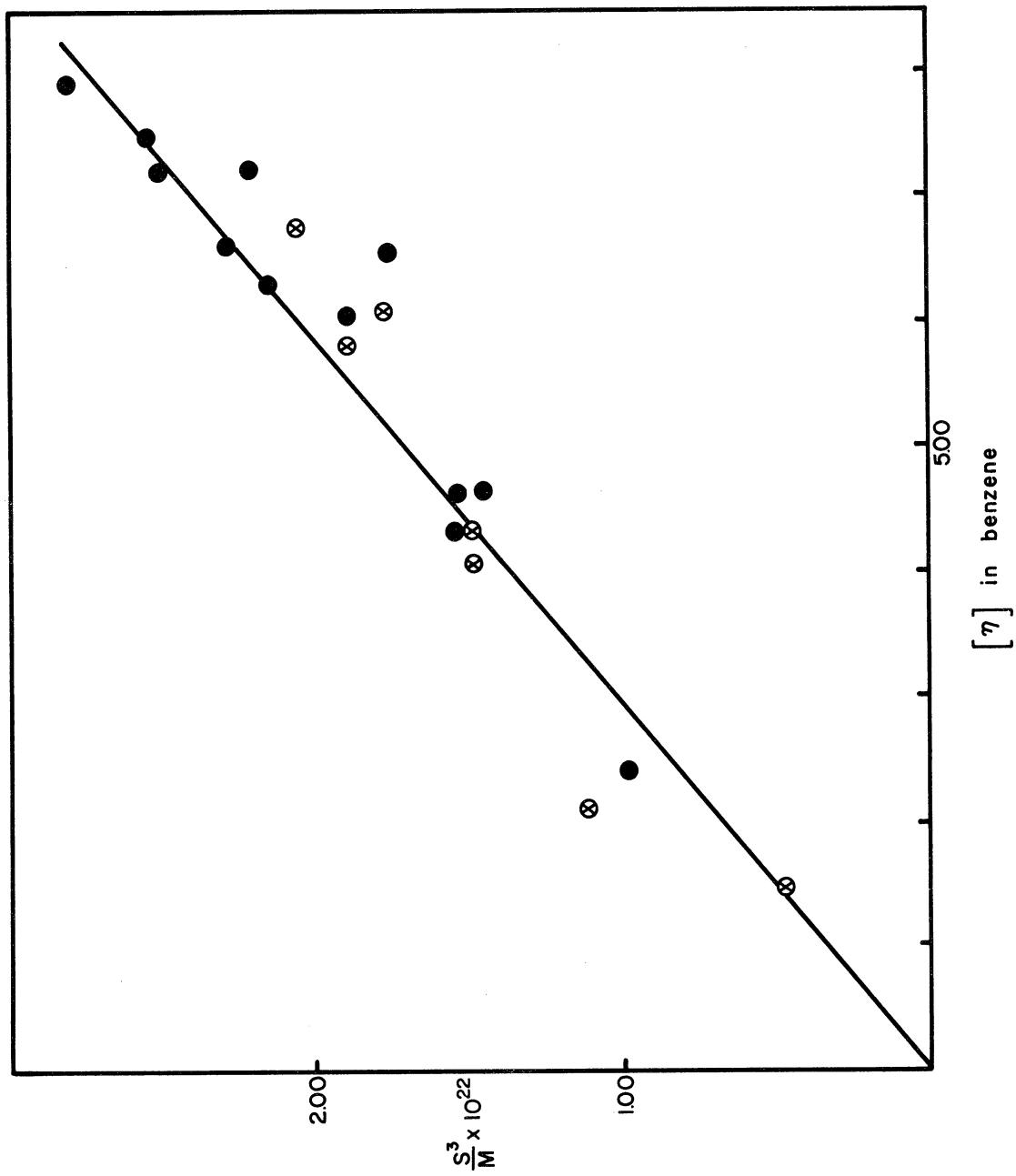


Fig. 4 Relation between Intrinsic Viscosity (in Benzene) and  $S^3/M$

TABLE I  
LIGHT-SCATTERING DATA\* FOR FRACTIONS OF LINEAR POLYSTYRENE

Solvent	Fraction	$[\eta]$ benzene, dl/g	$R(x 10^{-3}),$ $A^\circ$	$M(x 10^{-6})$	$\Phi(x 10^{-21})$	$A_2(x 10^4)$
Benzene	F21	(1.48)	0.637	0.334	2.50	4.3
"	F7B3	2.10	0.995	0.524	1.45	3.5
"	F5A2	4.05	1.50	1.33	2.12	3.0
"	F3A2	4.37	1.65	1.76	2.22	2.6
"	Q2B2	5.82	1.91	2.20	2.38	4.2
"	Q2B2	5.82	1.90	2.29	2.52	3.2
"	T8	(6.75)	2.11	2.76	2.55	4.4
"	RP-3-2**	(4.53)	1.63	1.50	1.66	5.4
"	RP-3-2	(4.53)	1.62	1.43	1.53	3.7
Butanone	Q2B2	5.82	1.41	2.14	2.60	2.2
"	F5A2	4.05	1.24	1.32	1.72	1.6
Average	$\Phi$ (benzene)				$= 2.2 \times 10^{21}$	
Average	$\Phi$ (butanone)				$= 1.9 \times 10^{21}$	
Average	$\Phi$ expected (14, p. 616)				$= 2.1 \times 10^{21}$	

\* Data given in parentheses have been calculated from data obtained with a different solvent by means of the equation given in reference 9.

\*\* A primary fraction (see section on materials).

TABLE II  
LIGHT-SCATTERING DATA FOR GRAFT POLYMERS

Sample*	Solvent	$R(x 10^{-3}), A^\circ$	$M(x 10^{-6})$	$\phi(x 10^{-21})$	$A_2(x 10^4)$
GC-140-1	Benzene	2.14	3.72	3.14	1.60
GC-140-2	"	1.80	2.58	3.47	1.28
GC-140-3	"	1.59	3.72	5.62	1.05
GC-210-1	"	2.19	3.68	3.29	0.79
GC-210-2	"	1.63	3.64	5.07	1.38
GC-210-3	"	1.14	1.22	2.56	1.55
GC-210-3	"	1.19	1.26	2.34	1.55
GC-211-1	"	2.24	4.07	3.75	0.0
GC-211-2	"	1.97	3.94	4.22	0.30
GC-211-2	"	2.06	3.79	3.55	0.10
GC-211-3	"	1.82	4.39	4.06	1.65
GC-230-1	"	1.95	4.71	6.18	0.75
GC-621	"	2.21	5.29	4.19	1.45
GC-140-3	Butanone	1.64	5.38	3.10	0.93
GC-210-3	"	1.16	3.33	3.43	1.06
GC-211-2	"	1.45	4.62	5.61	0.95

\* The final digit in the fraction number refers to the order of appearance of the fraction during fractionation; for example, GC-140-1 represents the first fraction obtained from the whole polymer GC-140.

\*\* Average of two values -- 4.55 and 4.78.



TABLE III  
FLORY CONSTANT,  $\Phi'$ , FOR GRAFT POLYMERS

Sample	$\Phi'^*$ ( $\times 10^{-21}$ )	$\Phi'_{(SF)}$ ( $\times 10^{-21}$ )
GC-140-1	31.7	38.8
GC-140-2	36.0	42.6
GC-140-3	36.7	54.5
GC-210-1	33.9	38.3
GC-210-2	34.2	53.1
GC-210-3	27.3	38.5
GC-211-1	32.4	32.9
GC-211-2	33.4	45.1
GC-211-3	31.7	53.3
GC-230-1	33.6	41.6
GC-621	42.8	61.4

Average  $\Phi'$  =  $33.9 \times 10^{21}$  or  $3.4 \times 10^{22}$

Average  $\Phi'_{(SF)}$  =  $45.4 \times 10^{21}$  or  $4.5 \times 10^{22}$

Average expected (assuming  $\Phi = 2.10 \times 10^{21}$ ) =  
 $30.9 \times 10^{21}$  or  $3.1 \times 10^{22}$

\* Values of  $g$  required for the calculation of  $\Phi'_{(SF)}$  were determined by the Stockmayer-Fixman method (16).

TABLE IV  
 VISCOSITY DATA FOR GRAFT POLYMERS

Sample	Solvent: benzene		Solvent: butanone		$\frac{g^{3/2}}{(\text{butanone})}$	g	g (SF) *
	$[\eta]$ (dl/g)	k'	$[\eta]$ (dl/g)	k'			
GC-140-1	6.38	0.36	3.07	0.40	0.853	0.90	0.78
GC-140-2	6.02	0.31	2.50	0.36	0.893	0.93	0.83
GC-140-3	4.55 4.78	0.34 0.35	1.96	0.24	0.909	0.67	0.47
GC-210-1	7.22	0.28	3.25	0.38	0.812	0.95	0.88
GC-210-2	4.62	0.32	2.11 2.07	0.36 0.33	0.594 0.594	0.71	0.52
GC-210-3	2.39	0.34	1.24	0.31	0.704	0.79	0.62
GC-211-1	7.95	0.38	3.97	0.36	1.02	1.0	1.0
GC-211-2	6.30	0.38	2.84	0.36	0.774	0.84	0.69
GC-211-3	4.28	0.36	2.11	0.33	0.528	0.65	0.46
GC-211-4	2.86	0.26	1.32	0.42	--	--	--
GC-230-1	7.50	0.26	3.53	0.30	0.844	0.89	0.78

\* Calculated by the method of Stockmayer and Fixman (16).

TABLE IV (CONT'D)

Sample	Solvent: benzene $\frac{[\eta]}{[\eta]} \text{ (dl/g)}$	Solvent: butanone $\frac{[\eta]}{[\eta]} \text{ (dl/g)}$	$\frac{g^{3/2}}{g}$ (butanone)	g	g <sup>*</sup> (SF)
GC-230-2	4.72	0.37	2.21	0.33	--
GC-230-3	4.09	0.35	2.06	0.39	--
GC-230-4	3.51	0.35	1.59	0.39	--
GC-621	6.59	<u>0.39</u>	2.40	<u>0.43</u>	0.67
	Ave: 0.34			Ave: 0.36	0.48

\* Calculated by the method of Stockmayer and Fixman (16).

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